Additie van water aan 1-alkynylethers. Knetiek en mechanisme

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SUMMARY.

This thesis deals with a study of the mechanism of the acid catalyzed addition of water to 1-alkynyl ethers:

$$R'C{\equiv}C{-}OR + H_2O \longrightarrow R'CH_2COOR$$

After an introduction in chapter 1, it is shown in chapter 2 that the addition of water to methoxyethyne, ethoxyethyne and propoxyethyne is subject to general acid catalysis. In addition to $H_3O^{\oplus}$-ions, $H_2PO_4^{\ominus}$-ions also contribute to the total rate of reaction (tables 2.1 and 2.2). The reactions were carried out in aqueous solution at 25°. The acidity was maintained at a constant value by a buffer of either

$$KH_2PO_4\text{-}Na_2HPO_4 \text{ or } NaH_2AsO_4\text{-}Na_2HAsO_4.$$

The rates were determined dilatometrically. The rate of reaction of ethoxyethyne was also determined from the change of the vapour pressure over the solution by means of a membrane manometer (table 2.3, figure 2.4). In order to calculate the rate constants, it was necessary to know the Henry's law constant, α, for ethoxyethyne, dissolved in water. The value of α is $3.58.10^{-4}$ mole/l^{-1}.mm Hg^{-1} (table 2.4). The solubility of ethoxyethyne in water at 25° amounts to 0.094 ± 0.001 mole/l or 6.59 ± 0.06 g/l (figure 2.5).

Some experiments with cis-$CH_3C{\equiv}C{-}O{-}CH{=}CHCH_3$ were carried out in H_2O and D_2O with $HClO_4$ as the catalyzing acid. For the kinetic isotope effect the value $k_{H_2O}/k_{D_2O} = 1.7$ was found (table 2.5). The addition of water to this compound was followed spectrophotometrically in the ultra-violet region. From infra-red spectra it appeared that the triple bond and not the double bond of $CH_3C{\equiv}C{-}O{-}CH{=}CHCH_3$ was hydrated during the kinetic measurements.

These facts indicate that a proton transfer to the triple bond is the first and rate-determining step of the reaction. An explanation for the high rate of reaction of these unsaturated ethers compared to ethyne or alkylethynes, is the considerable stabilization by resonance of the transition state, which resembles the carbonium ion:

$$R'CH=\overset{\oplus}{C}-OR \longleftrightarrow R'CH=C=\overset{\oplus}{O}R$$

In chapter 3 application of the activity postulate of GRUNWALD to the addition of water to $CH_3C\equiv C-OC_2H_5$ is described. A straight line is obtained when (log k_1 - log $f_H{}^{\oplus}$) is plotted against Yo for the reaction of this compound in 0.0040 N $HClO_4$ solution in 40 - 99.6 weight per cent ethanol-water mixtures at 25° (figure 3.1). This result suggest that a water molecule is not covalently bound in the transition state of the rate-determining proton transfer. Therefore, a concerted mechanism involving e.g. a cyclic transition state is also not probable. The rates of these reactions were measured spectrophotometrically in the ultra-violet region by means of a cell through which the solution from a reactor circulated at 25°. In this manner reactions with half-life-times of about fifteen seconds could be followed.

The above mentioned conclusion is supported by the $\Delta S^{\neq}$ values of three ethynyl ethers, calculated with the theory of the absolute reaction rates from the second-order rate constants at 25° and 50° (tables 2.2 and 3.3). The values of $\Delta S^{\neq}$ for the catalysis by hydronium ions lie between -1 and -10 e.u (table 3.4).

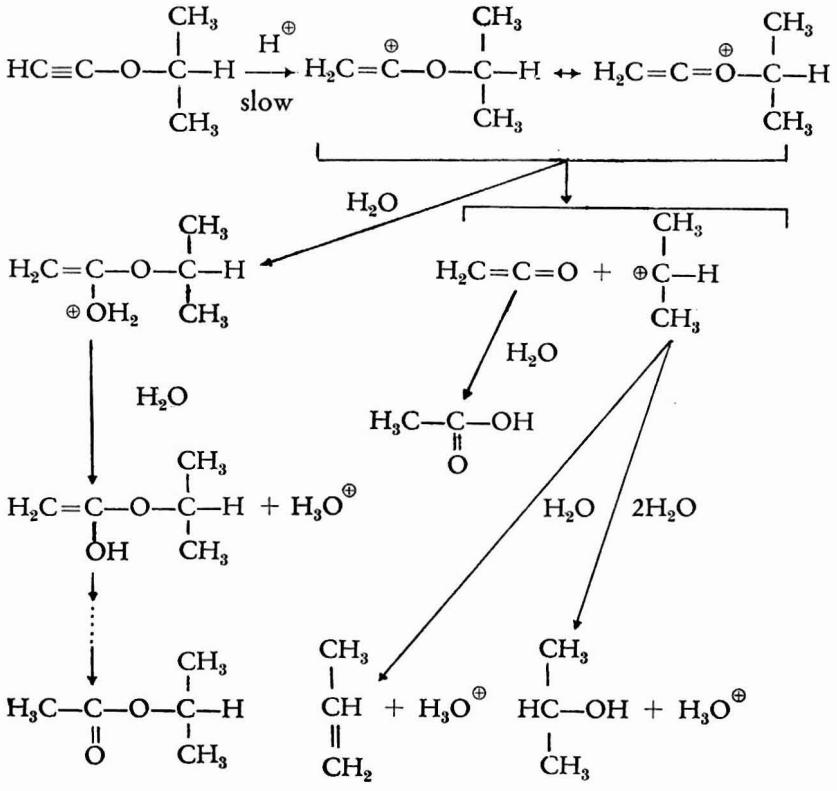
It is reasonable to assume that the hydration reaction proceeds along the following scheme:

$$HC\equiv C-OR + HA \longrightarrow H_2C=\overset{\oplus}{C}-OR + A^{\ominus} \quad \text{slow}$$

$$H_2C=\overset{\oplus}{C}-OR + H_2O \longrightarrow H_2C=\underset{\oplus OH_2}{C}-OR$$

$$H_2C=\underset{\oplus OH_2}{C}-OR + H_2O \longrightarrow H_3C-COOR + H_3O^{\oplus}$$

Chapter 4 deals with the acid catalyzed hydration of isopropoxyethyne and tert.butoxyethyne. It appeared, that during a reaction the pH of the buffer solution decreased. This phenomenon was explained by the formation of acetic acid. Alkyl-oxygen fission of the initially formed carbonium ion gives an alkyl carbonium ion and ketene which rapidly reacts with water to acetic acid. The hydration of these ethers is also subject to general acid catalysis (tables 4.1 and 4.2), again indicating that the protonation of the triple bond is rate-determining:



Thus, isopropoxyethyne and tert.butoxyethyne react in two ways: partly to the corresponding esters and partly to acetic acid and an alkyl carbonium ion. The hydration of isopropoxyethyne leads to approximately 12 per cent and that of tert.butoxyethyne

to approximately 61 per cent of acetic acid. The reactions were carried out in aqueous solutions, buffered with KH_2PO_4 - Na_2HPO_4 at 25°. The rates were measured by automatic titration of acetic acid with a dilute solution of sodium hydroxide.

In section 4.2 the rate constants of a series of ethynyl ethers HC≡C—OR are analyzed with the Taft equation:

$$\log k_R = \varrho^* \sigma_R^* + \text{constant}$$

For R = CH_3, C_2H_5, C_3H_7, i-C_3H_7 and t.C_4H_9 the polar substituent constant, ϱ^*, has a value of-6.2 in case the hydronium ion was the catalyzing acid, and a value of -8.4 in case the $H_2PO_4^{\ominus}$-ion was the catalyzing acid. These exceptionally low values of ϱ^* are a reflection of the large electron-donating properties of the OR group.From the close fit of the points to the straight lines (figures 4.2 and 4.3), it may be concluded that steric effects upon the rates are not present.

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